

Site-Specific Emission Rates Determination for Sixteen Degreasers

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Abstract

The present study has evaluated chlorinated solvent emission rates from 16 open-top vapor-phase industrial degreasers at 14 sites in Illinois and Wisconsin, USA. Simultaneously, twelve one-hour air samples from the workspaces were collected and analyzed for chlorinated solvents using NIOSH Method 1022. Solvent emission rates were calculated from the air sample concentrations from all sites using three appropriate mass balance models (completely mixed space mass balance, 2-point diffusion, and experimental mass balance). The models were applied and compared at sites where the sampling data supported emission rates calculation. The average workspace solvent concentrations and total emission rates were reported for all sites. The average site emission rates were in excellent agreement with published emissions for batch vapor-phase degreasers. At most sites, reasonably strong agreements were obtained between the three models, implying that they adequately estimated emissions. Emission rates determination is necessary to develop emission factors. The usefulness of the emission rates and emission factors approach is that when the data is applied, subsequent workspace changes can be made and potential exposures can be readily reproduced. The emission rates determined in this study can be used to predict mass emission rates for similar open-top vapor degreasing processes in other settings.

Keywords

Open-top Vapor Degreaser; Chlorinated Solvents; Area Concentrations; Mass Balance Models; Emission Rates

Introduction

In the United States, many industrial and manufacturing processes often include product cleaning steps in which chlorinated solvents are employed in vapor phase degreasing operations (U.S. EPA, 1995). The metal working industries are the major users of solvent degreasing, including, automotive, electronics, plumbing, aircraft,

refrigeration, and business machine industries (Turner and Crume, 1992). Halogenated solvents have been widely used to remove water-insoluble greases, fats, oils, waxes, carbon deposits, fluxes, and tars from metal parts prior to further treatment and use (U.S. EPA, 1995; Burgess, 1995). Typically, parts are cleaned prior to plating, painting, inspection, repair, assembly, heat treatment, and machining (Burgess, 1995). Generally, vapor degreasing uses chlorinated solvents such as trichloroethylene (TCE), methylene chloride (MC), perchloroethylene (PCE), 1,1,1-trichloroethane (TCA), carbon tetrachloride (CT), or chloroform.

Previous reports have indicated that most of the releases of chlorinated solvents into the atmosphere are as a result of vapour degreasing operations. A number of these chlorinated solvents, specifically TCE, have been detected in the ambient air, with the highest atmospheric levels occurring in urbanized and industrialized areas throughout the United States (ATSDR, 1997c). Additionally, these solvents present potential public health hazards including cancer and noncancer toxicity to the central nervous system, kidney, liver, immune system, male reproductive system, and the developing fetus (U.S. EPA, 2011).

Literature Review

Vapor-phase cleaning (also known as vapor degreasing) is commonly used to clean machined parts in metal working operations. The conventional vapor degreaser consists of a tank of solvent heated to its boiling point (U.S. EPA, 1989). The tank is designed to generate and contain solvent vapor which when heated, boils and rises to the level of the primary condenser, displacing the air inside the tank. The coils, generally located around the periphery of the inside walls of the cleaner, provide continuous condensation of the rising vapors and, therefore reducing vapor

emissions from the tank. Heavily soiled parts can be lowered into the boiling solvent and/or sprayed with warm solvent (Turner and Crume, 1992). The vapors condense on the parts, and the contaminants (e.g., oil) drain out with the condensate. The condensate drops into a sump which is heated to generate more vapors. Before reaching the sump, the condensate passes through a water separator which allows the solvent to flow back into the degreaser. This process continues until the workload reaches the same temperature as the solvent vapor. Complete cleaning occurs when no more solvent condenses on the parts leading to the withdrawal and cooling of the workload (U.S. EPA, 1989). Residual liquid solvent on the parts would rapidly evaporate during slow removal from the vapor zone and the solvent in the sump used until excess contaminants accumulate in the spent solvent. Alternatively, the spent solvent may be distilled by conventional means and reused (U.S. EPA, 1989).

Degreasing solvents typically contain chemical stabilizers to prevent acid formation and removal of contaminants from the bulk solution. Solvent vapors can be pulled or pushed out of the machine when work parts or baskets exit or enter the machine. Solvent loss reaches therefore the greatest when a "piston effect" is created, thus increasing the potential for workplace emissions. Previous studies on conventional OTVDs have documented that a large amount of the solvent (usually more than 90% in some cases) is lost through air emissions (U.S. EPA, 1995; Lemming et al, 2010). Typical characteristic of these solvents include their higher vapor pressures than air (USEPA, 1989; 1995). Additionally, solvent selection is often based on the solubility of the substance to be removed, toxicity, flammability, flashpoint, evaporation rate, boiling point, cost, and other properties of individual solvents (Turner, 1992).

Chlorinated solvents such as TCE are common contaminants in indoor air, ambient air, soil, and ground water due to their extensive and widespread use of solvents (U.S. EPA, 2011). TCE, a stable and colorless liquid with a chloroform-like odor has been commercially produced worldwide by chlorination of ethylene or acetylene since 1920s (U.S. EPA, 2011). TCE was used extensive as a degreasing solvent in metal-fabricating operations from the early 1920s through the 1970 s. In the 1970s the use of TCE was very limited due to growing environmental concerns and stringent regulations and in 1977 it was banned for use in cosmetics and as a food additive (Bakke et al., 2007).

Environmental contamination and human exposures have resulted from their use as cleaning agents and metal degreasers (U.S. EPA, 2004). The majority of contamination occurred mainly from evaporative losses during use, discharge to surface waters and groundwater, leaching from hazardous waste landfills into groundwater, and incidental addition to consumer products (ATSDR, 1997c). Previous surveys conducted by the U.S. Environmental Protection Agency (U.S. EPA, 2004; 2008) reported the presence of trichloroethylene in at least 460 of 1,177 hazardous waste sites listed in its National Priorities List. In the United States, chlorinated solvents and their natural biotransformation products are the most frequently observed groundwater contaminants. In addition, chlorinated solvents released into the atmosphere could be transported long distances to the troposphere, where they are degraded slowly by photooxidation (Turner and Crume, 1992). These solvents can subsequently diffuse to the stratosphere where photodegradation is rapid, and the chlorine free radicals that are generated may contribute to the destruction of the ozone layer.

A number of studies have documented workers' exposures in different industries where chlorinated solvents were employed in vapor phase degreasing. In the United Kingdom, a review of industrial applications involving chlorinated solvents from 1961 to 1983 was based on reported industrial gassing poisonings" (Burgess, 1995). The study concluded that out of 384 cases of poisoning, 288 were from TCE, 44 involved handling PCE, and 52 were from TCA. In 168 of the cases, the workers were found unconscious and 14 cases resulted in fatalities, with 10 of the fatalities occurring in confined spaces (Burgess, 1995). In the United States, the National Occupational Exposure Survey conducted by the National Institute for Occupational Safety and Health (NIOSH, 1990) from 1981 to 1983 estimated that 401,000 workers employed at 23,225 plant sites were exposed to TCE. According to NIOSH, the greatest exposures occurred during metal degreasing operations (NIOSH, 1990).

A NIOSH survey on 44 dry cleaning facilities showed PCE TWA exposures to machine operators ranging from 4 to 149 ppm (NIOSH, 1990). Additionally, the NIOSH survey estimated that 688,110 workers employed at 49,025 plant sites were potentially exposed to PCE (NIOSH, 1990) that is on the list of toxic chemicals subject to the reporting requirements of Section 313 of the Emergency Planning and Community Right-To-Know Act of 1986, otherwise

known as EPCRA (U.S. EPA, 2008). Other studies conducted by NIOSH during the same period showed that more than 58,000 to 1.5 million workers were at increased risk of exposures to halogenated solvents (NIOSH, 1990). NIOSH noted that workers in degreasing plants were particularly vulnerable to high levels of exposure from inhalation of vapors and/or skin absorption.

Aerosol propellants often contain up to 50% of methylene chloride or other chlorofluorocarbons. When released to the atmosphere, these aerosols would readily disperse so that persons living near production and use facilities or near hazardous waste sites had potentially increased risks of exposures (U.S. EPA, 2011). MC is a hazardous chemical listed on the U.S. EPA Toxic Releases Inventory (Gavaskar, Olfenbuttel, and Jones, 1993). In 1992, the 93 signatories to the Montreal Protocol, an International Agreement to control ozone-depleting substances, agreed to ban TCA and certain chlorocarbons by 1996, four years earlier than previously agreed (ATSDR, 1993). Air emissions are a concern for metal finishers because many of the solvents used in vapor degreasing have been targeted by the EPA in the 33/50 Program, which requires 33% reduction by 1992 and 50% reduction by 1995 (Gavaskar, Olfenbuttel, and Jones, 1993). Air pollution control measures for chlorinated solvent cleaners often involve specific equipment design features and the implementation of good operating practices (U.S. EPA, 1995). These design requirements are necessary to define effective control options to fulfil the intended purpose.

In 1978, the United States and Canada jointly banned the manufacture of chlorofluorocarbons (CFCs) for aerosols (U.S. EPA, 1995). On December 2, 1994, the U.S. EPA (1995) promulgated the National Emission Standards for Hazardous Air Pollutants (NESHAPs) for halogenated solvent cleaners. (U.S. EPA, 1995). These standards, specifically regulate the use of solvents that contain 5% or more by weight of any one or a combination of methylene chloride, carbon tetrachloride, chloroform, perchloroethylene, 1,1,1-trichloroethane, and trichloroethylene. The U.S. EPA (2008) has also developed a "Solvent Alternative Guide" that meets the cleaning needs of many industries where halogenated solvents are employed in degreasing. The U.S. EPA believes that the decision to seek out safer alternative solvents is due to the strong restrictions or prohibitions imposed on the manufacture of these halogenated solvents. The general requirement for alternative solvents is that it

will reduce overall risk to human health and the environment (U.S. EPA, 2008). It may also be a result of corporate objectives aimed at limiting worker exposure, minimizing cost of storage, handling, management, and disposal of hazardous wastes, and complying with regulations to foster a public image (USEPA, 2008). The U.S. EPA (1994), under NESHAPs, mandates the use of maximum achievable control technology (MACT) for each major source category emitting hazardous air pollutants (HAPs). New developments in vapor degreasers design has created the potential of nearly total elimination of HAPs emissions during degreasing operations. Chlorinated solvents are subject to the reporting requirements of sections 313 of the Superfund Amendments and Reauthorization Act (SARA) Title III of 1986 and section 6607 of the Pollution Prevention Act (U.S. EPA, 1995).

According to a report by Gavaskar, Olfenbuttel, and Jones, (1993), the low emission vapor degreaser reduced vapor emissions by more than 99% compared to the estimated air emissions from a typical conventional open top vapor degreaser (560 lb of parts/hr capacity, with a 0.75 freeboard ratio, primary cooling coil, electric hoist, and no lip exhausts). Compared to an average emission rate of about 1.6 lb/hr for a standard open top vapor degreaser, Cornstubblet. al., (1995) reported that the low emission vapor degreaser equipment showed a 74% improvement over conventional emission rates. Previous studies on conventional open top vapor degreasers showed that a large part of the solvent (more than 90% in some cases) is lost through air emissions and that the enclosed vapor degreaser has the potential for significantly reducing solvent use by preventing air emission losses (U.S. EPA, 1995).

Air emissions are typically workload-related, caused either by drag-out of solvent on the workload itself (and subsequent vaporization) or by disturbance in the air-vapor interface during entry and exit of the workload (Gavaskar, Olfenbuttel, and Jones, (1993). The U.S. EPA (1995) reported an emission factor of 9.5 Mg/yr/unit (10.5 ton/yr/unit) of solvent loss from open top vapor degreasers units in operation throughout the United States. The uncontrolled solvent emission factor, when the surface area and duty cycle are considered, was 0.71 kg/hr/m² (0.15 lb/hr/ft²). The report also noted that solvent consumption data was more accurate in determining emission estimates than any of the other factors presented and that emissions were generally higher for manufacturing units than

that for maintenance units. A number of recent studies have used life cycle assessment to evaluate the environmental impacts of remediation of a site contaminated by TCE (Lemming et al, 2010). The authors compared *in situ* bioremediation by enhanced reductive dechlorination, *in situ* thermal desorption, and excavation of the contaminated soil followed by off-site treatment and disposal. Their results showed that enhanced reductive dechlorination remarkably reduced the life-cycle impacts of remediation when compared to the other two options.

Other studies have reported several useful approaches that have been successfully applied to characterize workroom emissions (Wadden et al., 1994; Conroy et al., 1995). Typically, most of these studies used measured area concentration and ventilation data with simultaneous observations of source activities to calculate emission rates and emission factors. By the application of mass balance models appropriate for the geometry and patterns of work performed in a particular space, concentration and ventilation measurements were transformed into emission rates (mass of pollutant released per unit time). Additionally, when calculated emission rates were used in conjunction with source activity observations, emission factors (mass of pollutant released per unit of source activity) were developed.

Wadden et al., (1989) had previously characterized emission factors related to source activity for TCE degreasing and chrome plating processes at a small engine parts fabrication plant. The evaluation provided examples of how to estimate process emission factors from activity and air concentration data. A previous study by Wadden et al., (1991) used a Fick's law diffusion approach to develop emission factors for two production vapor degreasers fitted with functioning local exhaust hoods. Their results were consistent with field observations and confirmed that the two-point diffusion model is appropriate for characterizing emissions from similar point sources indoors. The main advantage of the emission factors approach is that the effect of the particular interior space from which the data were collected is removed from the description of the source (Wadden, et al, 1994). Another advantage is that it provides a quantitative basis for the development of engineering controls (Iyiegbuniwe. and Conroy, 1995). The main objectives of this study were to calculate appropriate mixing factors and determine emission rates for 16 vapor degreasers at 14 sites.

Materials and Methods

Facility Description

This study evaluated vapor degreasing operations during normal operating conditions at 14 private industrial metal fabrication, metal finishing, electroplating, and electronics industries in Illinois and Wisconsin, USA. Degreasing was performed to remove cutting oils, fluxes, waxes, and other grease from work parts prior to grinding, plating, machining, inspection, repair, assembly, and shipping. Trichloroethylene, methyl chloroform, perchloroethylene, and methylene chloride were used in cleaning work parts. Trichloroethylene was employed in thirteen degreasers while each of the other three applications used methyl chloroform, perchloroethylene, and methylene chloride, respectively. Metal fabrication, which involved producing parts on large stamping mills, was carried out at sites 1a, 2a, 3a, 7a, 8a, 8b, and 9a. Sites 4a, 10a, 10b, and 13a were metal finishing shops where grinding and polishing of work parts occurred. A large paint line, where cleaned parts were painted, was also present at site 13a. Electroplating was performed at sites 6a, 6b, and 14a. Chrome plating was the primary operation carried out on all degreased metal parts. Sites 11a and 12a were electronics manufacturing shops. In these facilities, electronic chips or printed circuit boards were soldered in a reflow oven, and this was followed by degreasing to remove excess solder flux from the chips or boards.

Data Collection

Sampling was conducted under normal operating conditions over one or two 8-hour shifts for each degreasing site. Solvent concentrations, air flow rates, source activities, and other measurements were collected. Area concentrations of solvents were measured at one hour intervals in both the local exhaust ventilation (LEV) duct and the workspace (at various distances from each degreaser). All air samples were collected with charcoal adsorption tubes connected by Tygon tubing to portable sampling pumps. Air flows were controlled at approximately 0.2 liters per minute using each pump's internal needle valve. Flow rates were verified with a calibrated rotameter at the beginning, middle, and end of each one hour sampling period. Additional solvent samples were collected in 30 minute intervals in the LEV duct and at measured distances from the degreaser during idling conditions. All samples were analyzed by gas

chromatography coupled with flame ionization detector in accordance with NIOSH Analytical Method 1022 (NIOSH, 1984)

Air flow rates in the local exhaust hoods were measured in the duct using a Pitot tube connected to a manometer. In cases where the air velocity in the duct was too low to be accurately determined with a Pitot tube and manometer, the slot hood area and slot velocity were determined using a tape measure and a calibrated TSI Model 8350 Velocicalc hot film anemometer, respectively. Ventilation measurements were also made through room openings (i.e. doors, windows) using a TSI Model 8350 Velocicalc hot film anemometer. General ventilation supply and exhaust air flows were also determined at sites with mechanical supply and return air systems using an Alnor Balometer. Mechanical ventilation consisted of LEV on the degreaser and at other operations such as plating tanks and grinding wheels. Only two of the fourteen sites (11a and 12a) were provided with mechanical make-up air and general ventilation.

Mathematical Models

Workspace emissions of pollutants can generally be characterized with the application of appropriate mathematical models (Iyiegbuniwe and Conroy, 2010) which can describe indoor concentration patterns created by both outdoor and indoor emission sources. The use of these models typically depends on the nature of collected data and the basic assumptions underlying the application of the particular model. In this study, the completely mixed space (CMS), the two-point diffusion (2PT), and the experimental mass balance (EMB) models were the three models of interest in calculating emission rates for some or all of the 16 degreasers. Emission rates can be derived from solvent consumption data for each degreasing operation under consideration. In this study, each of the three models was based on a mass balance approach to estimate the pollutants in a specified volume. The methods applied depended on how specific contributions from a particular emission source were characterized.

1) Completely Mixed Space (CMS) Model

Area concentration and ventilation measurements were used in a CMS model to calculate emission rates. The concept of the CMS model is based on the measurements of average concentrations and air flow rates through the workspace. The one

compartment mass balance model is expressed as equation (1).

$$S_{cms} = \frac{C k q - [\frac{C_s V}{t_{av}}] [1 - \exp(-\frac{k q}{V} t_{av})]}{1 + [\frac{V}{k q t_{av}}] [\exp(-\frac{k q}{V} t_{av}) - 1]} \quad (1)$$

Where:

- S_{cms} = workspace mass emission rate (mass/time)
- C = average concentration (mass/volume)
- C_s = instantaneous concentration of pollutant at start of the sampling (mass/volume)
- V = volume of the workspace (volume)
- t_{av} = average sampling time (time)
- q/v = air change rate (1/time)
- k = mixing factor (varies between 0 and 1).

The S_{cms} term in the above equation represents a net emission rate, i.e., actual release or deposition of vapor in the space (36). Since the operations were carried out on hard concrete surfaces, without fabric rugs or floor mats, it was assumed that vapor deposition was negligible compared to actual release. At steady state, the CMS model is expressed as equation (2).

$$S_i = k C_{ss} Q \quad (2)$$

Where:

- S_i = workspace mass emission rate (mass/time)
- K = mixing factor to account for the incomplete mixing of ventilation air with room air
- C_{ss} = steady state concentration (mass/volume)
- Q = ventilation rate through the workspace (Volume/time).

The assumptions in the CMS model are:

- a. There is perfect mixing in the space, both spatially and temporally.
 - b. The emission rate of pollutants is constant.
 - c. The concentration of pollutants in the dilution air is negligible.
 - d. All pollutants are introduced into the space only through emission processes.
 - e. All pollutants are removed from the workspace only through general ventilation.
- The above approach was used to estimate emissions from TCE vapor degreasers and chrome plating processes, emissions from lead paint during bridge renovation (Iyiegbuniwe and Conroy, 2010), and to calculate hood efficiencies of vapor degreasers under operating conditions (Conroy et al, 1995).

2) Two-Point Diffusion Model

The basic assumption underlying the application of the two-point diffusion (2PT) model is that a point source emits pollutants at a steady rate into an infinite hemispherical space. Other assumptions of the model are that the diffusion of contaminants follows Fick's Law of Diffusion and neglects deposition. Fick's Law states that for a point source emitting at steady state into an infinite space, the flux of emitted contaminants through an area in space perpendicular to flow is proportional to the product of the change in concentration with distance from the source and the molecular diffusivity (Wadden, et al, 1989; 1991). For indoor air pollution applications, the eddy diffusivity is more appropriate than molecular diffusivity (Franke, Wadden and Scheff, 1989). A solution to the mass balance on a system described above is given by Carslaw and Jaeger (1959) as equation (3).

$$C = \left(\frac{S_i}{2\pi Dr} \right) \operatorname{erfc} \left(\frac{r}{(4Dt)^{0.5}} \right) \quad (3)$$

Where:

C = mass concentration (mass/volume)

r = radius of the hemisphere from the point source (length)

t = sampling time (time)

D = eddy diffusivity (area/time)

S_i = workspace mass emission rate (mass/time)

erfc = error function complement (dimensionless)

The error function complement, (or 1 - error function readily obtained from reference tables) (Abramowitz and Segun, 1965) is expressed as equation (4):

$$\operatorname{erfc}(y) = 1 - \frac{2}{\pi^{0.5}} \int_0^y \exp(-x^2) dx \quad (4)$$

The integration of equation (3) gives the appropriate form needed to characterize average area concentrations (C_{av}), collected over a sampling time. Thus, by collecting simultaneous measurements of concentration at two different distances, r_1 and r_2 , the integral form of Equation (3) gives two independent equations as follows:

$$C_{av,r_1} = \frac{\left(\frac{S_i}{2\pi Dr_1} \right) \int_0^{t_{av}} \operatorname{erfc} \left(\frac{r_1}{(4Dt)^{0.5}} \right) dt}{t_{av}} \quad (5)$$

$$C_{av,r_2} = \frac{\left(\frac{S_i}{2\pi Dr_2} \right) \int_0^{t_{av}} \operatorname{erfc} \left(\frac{r_2}{(4Dt)^{0.5}} \right) dt}{t_{av}} \quad (6)$$

Equations (5) and (6) can be solved simultaneously for eddy diffusivity, D, and mass emission rate, S_i , using a trial and error approach. This approach has been used to calculate emission rates for two vapor phase degreasers (Wadden et al, 1989).

3) Experimental Mass Balance Model

The EMB model is based on measurements of concentrations and flow rates at all entry and exit points in the workspace, and therefore giving a measure of total (workspace + LEV) emission rates. The assumption of this model lies in the fact that the mass flow into the space plus any mass generated in the space must equal the mass flow out of the space plus accumulation of mass in the space. For a steady state system that defines mass flow as the product of volumetric flow rate and mass concentration, the emission rate is expressed as S_{EMB} equation (7) below.

$$S_{EMB} = \sum_{i=1}^n (Q_{oi} C_{oi}) - \sum_{j=1}^n (Q_{ij} C_{ij}) \quad (7)$$

Where:

S_{EMB} = mass balance emission rate (mass/time)

Q = general ventilation rate into (Q_{ij}), or out of (Q_{oi}) the workspace (mass/time)

C = workspace concentration (mass/volume)

Results and Discussions

Hourly interval solvent concentrations and ventilation measurements were determined for the workspace and LEV ducts. The results are summarized and presented in Tables 1 and 2. The overall average workspace concentration of TCE ranged from 3.33 ppm (site 6a) to 103 ppm (site 6b). The average concentration of methyl chloroform (site 1a), PCE (site 9a), and methylene chloride (site 12a) were 35.1 ppm, 1.71 ppm, and 13.0 ppm, respectively. Average LEV duct concentrations of TCE ranged from 21.1 ppm (site 6a) to 635 ppm (site 8b). Other solvents were 407 ppm, 107 ppm, and 47.7 ppm for methyl chloroform, PCE, and methylene chloride, respectively.

Workspace and LEV emissions were reasonably correlated with each other, indicating that they were affected by common factors or process variables. However, there were additional factors acting independently to produce workspace emissions.

TABLE 1 WORKSPACE AND LEV DUCT CONCENTRATIONS

Site	Interval	Interval Concentration at Sampling Locations (ppm)					Avg Conc (ppm)	Duct Conc (ppm)
		A	B	C	D	E		
1a	Day 1 Avg	64.4	40.5	21.9	99.5	na	37.8	746
	Day 2 Avg	34.9	26.1	28.2	22.6	39.7	32.4	68.2
	Overall Avg	49.7	33.2	25.1	61.1	19.8	35.1	407
2a	Day1 Avg	4.02	na	3.25	5.27	1.62	3.38	169
	Day2 Avg	4.59	3.05	3.65	2.63	na	3.48	221
	Overall Avg	4.31	1.53	3.45	3.95	0.81	3.43	195
3a	Day1 Avg	10.6	6.11	5.39	4.18	na	6.89	117
	Day2 Avg	7.17	6.77	4.92	4.22	na	5.77	114
	Overall Avg	8.89	6.43	5.15	4.21	na	6.33	116
4a	Interval 1	11.8	5.53	5.81	8.12	na	7.81	141
	Interval 2	21.8	9.04	11.2	17.1	na	14.76	223
	Interval 3	0.88	1.67	1.68	1.82	na	1.51	66.7
	Overall Avg	11.5	5.41	6.23	8.98	na	8.03	143
6a	Day1 Avg	5.13	1.75	1.74	na	na	3.07	10.6
	Day2 Avg	5.69	2.91	2.19	na	na	3.59	31.7
	Overall Avg	5.41	2.33	1.96	na	na	3.33	21.1
6b	Day1 Avg	9.07	1.85	9.03	na	na	6.65	327
	Day2 Avg	590	3.62	6.76	na	na	200	319
	Overall Avg	300	2.74	7.9	na	na	103	322
7a	Day1 Avg	45.8	56.9	51.6	na	na	51.4	282
	Day2 Avg	58.5	51.5	58.6	na	na	56.2	265
	Overall Avg	52.1	54.2	55.1	na	na	53.8	273
8a	Day1 Avg	31.6	17.1	6.62	na	52.1	33.6	251
	Day2 Avg	91.6	29.1	7.6	na	16.4	45.7	592
	Day3 Avg	72.1	25.6	7.4	na	16.2	37.9	601
	Overall Avg	65.1	23.9	7.2	na	28.2	39.1	481
8b	Day1 Avg	31.8	23.7	15.3	na	na	27.8	763
	Day2 Avg	53.3	191	25.1	na	na	122	625
	Day3 Avg	42.4	25.5	27.9	na	na	33.9	516
	Overall Avg	42.5	80.1	22.8	na	na	61.2	635
9a	Day1 Avg	3.08	2.02	1.52	1.66	na	2.07	121
	Day2 Avg	1.42	1.77	1.31	0.89	na	1.35	93.6
	Overall Avg	2.25	1.91	1.41	1.27	na	1.71	107
10a	Day1 Avg	58.6	9.91	3.39	na	na	23.9	93.8
	Day2 Avg	9.33	9.25	na	na	na	9.29	62.2
	Overall Avg	33.9	9.58	1.67	na	na	16.6	78.1
10b	Day1 Avg	57.8	23.3	3.82	na	na	28.3	16.5
	Day2 Avg	38.8	30.2	2.21	na	na	23.7	40.4
	Overall Avg	48.3	26.7	3.01	na	na	26	28.5
11a	Day1 Avg	10.6	0.03	0.03	na	0.17	2.7	197
	Day2 Avg	27.1	5.95	7.89	na	2.9	10.9	154
	Overall Avg	18.9	2.99	3.96	na	1.53	6.83	175
12a	Day1a Avg	8.4	4.7	5.6	na	na	6.23	13.1
	Day1b Avg	32.1	28.1	26.8	na	na	28.9	91.4
	Day2 Avg	4.6	3.46	3.4	na	na	3.82	38.7
	Overall Avg	15.1	12.1	11.9	na	na	13.1	47.7
13a	Day1 Avg	36.1	2.23	2.14	2.29	na	10.7	70.9
	Day2 Avg	31.1	2.11	2.12	2.03	na	8.44	53.6

	Overall 1 Avg	33. 6	2.1 7	2.1 3	2.1 6	na	9.56	62.2
14 a	Day1 Avg	37. 1	6.3 9	5.1 5	3.8 1	na	13.2	221
	Day 2 Avg	32. 7	5.4 8	4.8 7	4.1 1	na	11.8	151
	Overall 1 Avg	34. 9	5.9 4	5.0 1	3.9 6	na	12.5	186

TABLE 2 WORKSPACE AND LEV DUCT AIRFLOW RATES

Site	Day	Location	Airflow Rate	
			(m ³ /min)	(cfm)
1a	Day 1&2	Workspace	219	7,720
		LEV Duct	14.1	499
2a	Day 1&2	Workspace	577	20,380
		LEV Duct	21.4	757
3a	Day 1&2	Workspace	440	15,520
		LEV Duct	18.3	646
4a	Day 1&2	Workspace	389	13,720
		LEV Duct	23.7	838
6a	Day 1&2	Workspace	382	13,480
		LEV Duct	24.6	869
6b	Day 1&2	Workspace	354	12,510
		LEV Duct	11.8	416
7a	Day 1&2	Workspace	24.5	864
		LEV Duct	6.54	231
8a+b	Day 1&2	Workspace	478	16,870
		LEV Duct	70.6	2,492
9a	Day 1&2	Workspace	22.9	810
		LEV Duct	22.9	810
10a+b	Day 1	Workspace	917	32,380
		LEV Duct	29.6	1,050
	Day 2	Workspace	509	17,980
		LEV Duct	34.3	1,210
11a	Day 1&2	Workspace	na	na
		LEV Duct	10.2	359
12a	Day 1&2	Workspace	219	7,740
		LEV Duct	14.9	526
13a	Day1	Workspace	765	27,020
		LEV Duct	2.95	104
	Day 2	Workspace	765	27,020
		LEV Duct	3.17	112
14a	Day 1&2	Workspace	151	5,340
		LEV Duct	16.9	595

na = not available

Site averages were in good agreement with previously published values for batch vapor degreasers (Turner and Crume, 1992; USEPA, 1995). The results of the Pearson Correlation matrix for the three mass balance models (CMS, 2PT, and EMB) are summarized in Table 3 below. The 2PT model estimated emission rates higher than those estimated by the CMS model ($k = 0.3$) at some sites. Additionally, the 2PT model did not converge to physically realistic diffusivities at some sites, but specifically applied at site 11a for the determination of emission rates because the collected data did not support the use of the CMS model. The

linear relationship between the CMS and 2PT models was reasonably strong at most sites, implying that emissions were adequately being estimated. The EMB model, also showed very good agreement with both the CMS and 2PT models. Overall, emission rates developed using the CMS model provided more data than that using either the 2PT or EMB model.

TABLE 3 PEARSON CORRELATION MATRIX FOR THE MASS BALANCE MODELS (CMS, 2PT, AND EMB)

Site		CMS	2PT	EMB
1a	CMS	1.00		
	2PT	0.80	1.00	
	EMB	na	na	na
2a	CMS	1.00		
	2PT	0.09	1.00	
	EMB	na	na	na
3a	CMS	1.00		
	2PT	0.37	1.00	
	EMB	na	na	na
4a	CMS	1.00		
	2PT	0.99	1.00	
	EMB	na	na	na
6a	CMS	1.00		
	2PT	0.51	1.00	
	EMB	na	na	na
6b	CMS	1.00		
	2PT	0.48	1.00	
	EMB	na	na	na
7a	CMS	1.00		
	2PT	0.90	1.00	
	EMB	na	na	na
8a+b	CMS	1.00		
	2PT	0.98	1.00	
	EMB	0.76	0.59	1.00
9a	CMS	1.00		
	2PT	0.34	1.00	
	EMB	na	na	na
10a+b	CMS	1.00		
	2PT	0.09	1.00	
	EMB	0.01	0.95	1.00
12a	CMS	1.00		
	2PT	0.97	1.00	
	EMB	0.98	0.99	1.00
13a	CMS	1.00		
	2PT	0.61	1.00	
	EMB	na	na	na
14a	CMS	1.00		
	2PT	0.97	1.00	
	EMB	na	na	na
All Sites ^a	CMS	1.00		
	2PT	0.44	1.00	1.00
	EMB	0.92	0.95	

Table 4 describes and compares the present study emission rates with the U.S. EPA's (1977) three month average monthly emission limit of 150 kg/m²/month for batch vapor degreasers. The result showed that this limit was readily met at 5 of the 14 sites. Of the 9 sites that exceeded the limit, five sites had total emissions that were at least 50% over the limit. Furthermore, of

these 5 sites, 3 sites (6b, 8a+b, and 11a) had total emissions that were five, two, and three times the U.S. EPA's limit. Site 6b which recorded the highest average workspace concentration for TCE (103 ppm) also presented the highest overall emission rates. These results are in good agreement with worker exposure data reported by NIOSH (1990) which showed mean TWA concentrations of 50 to 100 ppm. Higher than normal workplace concentrations were attributed to poor workplace practices (improper operating procedures, negligence with regards to equipment maintenance or repair) and inadequate engineering controls (NIOSH, 1990).

TABLE 4 COMPARISON OF STUDY EMISSIONS WITH EPA'S MONTHLY EMISSION LIMIT

Site	Facility Type	Tank Area ^a ft ² (m ²)	Total Emission ^b (g/min)	Total Emission ^c kg/month	Emission Limit ^d kg/month	% of EPA's Limit
1a	MFN	13.9 (1.30)	32.2	302	195	155
2a	MFN	9.32 (0.87)	25.7	241	130	185
3a	MFN	12.6 (1.17)	15.5	145	176	83
4a	MFS	10.4 (0.97)	23.0	215	145	149
6a	EPG	10.7 (0.99)	5.47	51.2	148	35
6b	EPG	9.8 (0.91)	75.7	709	136	522
7a	MFN	10.0 (0.93)	11.6	109	139	78
8a+b	MFN	81.8 (7.6)	243	2,280	1,140	200
9a	MFN	16.7 (1.55)	17.6	165	233	71
10a+b	MFS	19.9 (1.85)	34.5	323	278	116
11a	ENS	2.05 (0.19)	12.7	119	28.5	416
12a	ENS	7.53 (0.70)	5.45	51.0	107	48
13a	MFS	6.03 (0.56)	12.8	120	83.3	144
14a	EPG	12.5 (1.16)	19.3	181	173	104

^aTotal surface area of each degreaser by site (i.e., solvent-air interface area)

^bAverage total emissions determined from the sum of workspace and LEV emissions

^cAssumes a 6-day operating week (26 days/month). Average total emissions calculated from workspace and LEV sampling results collected for a 12-hr period over two days.

^dEPA's 3-month average monthly emission limit of 150 kg/m²/month for vapor degreasers.

MFN = Metal Fabrication; EPG = Electroplating; MFS = Metal Finishing; ENS = Electronics

In general, newer models of solvent cleaning and degreasing machines are equipped with covers (i.e., working-mode or idling-mode) to assist the reduction of diffusion losses and emissions (U.S. EPA, 1995; 2008). Previous tests conducted by the EPA indicated that automatic lids could reduce solvent loss by a factor of 50 percent or more (U.S. EPA, 2008). The best emission reduction technique has been reported to be the

minimization of cross-current drafts at the lip of the degreaser (Turner, 1992).

Conclusions

In this study, emission rates were determined based on simultaneously collected area chlorinated solvent concentrations and ventilation measurements for 16 vapor degreasers at 14 sites. The overall average degreaser emission rate determined in this study was 23 g/m²/min, with a range from 5.5 g/m²/min at site 12a with a single degreaser to 83.2 g/m²/min at site 8a+b with two degreasers. Site averages were in excellent agreement with previously published values for batch vapor degreasers (U.S. EPA, 1995). Emission rates developed using the CMS model ($k=0.3$) provided more data than that using either the 2PT or EMB models. At some sites, the 2PT model did not converge to a physically realistic diffusivity, but useful to distinguish emissions from two adjacent degreasers located in the same workspace. The EMB model generally estimated total emissions at the three sites where it was applied. However, the three mass balance models showed reasonably good agreement with each other in determining emissions at most sites.

Workspace and LEV emissions were reasonably correlated with each other, indicating that they were affected by common factors or process variables. However, there were additional factors acting independently to produce other workspace emissions. The study has shown that open top vapor degreasers relate significantly to varying operating procedures and activities. In addition, site-specific activities were also shown to influence workspace emissions. Further analysis with simple multiple variable model did not significantly explain emissions more than the individual activity variables. The U.S. EPA (1977; 1989) had previously reported that solvent carryout emissions would be reduced if work parts are drained for at least 15 seconds and that most open top vapor degreasers' emissions were due to diffusion and convection losses. These emissions can be reduced by use of an automated cover, by using a manual cover regularly, and by optimizing workloads. Spraying at low pressure will also reduce solvent loss from these types of degreasers. In general, chlorinated solvents emissions from open top vapor degreasers are highly influenced by operating variables in the workspace.

To reduce workplace exposures and environmental emissions, it is recommended that adequate

engineering control strategies are considered. The selection of appropriate control technologies should consider the potential to retrofit existing vapordegreasers. Retrofit technology is important to reduce potential installation costs for new equipment and facilities. There is a need to constantly establish and maintain adequate capture efficiency of local exhaust slot hoods used for vapor degreasing operations. Alternatively, the degreasers could be completely enclosed and automated with functioning vacuum technology systems for emission control. Industrial vapor degreasing processes constitute the largest single use for solvents (particularly chlorinated solvents that contribute to the destruction of the ozone layer), with as much as 90% of vapor degreasing solvents lost through air emissions (U.S. EPA, 2011).

In general, newer models of solvent cleaning and degreasing machines are equipped with covers (i.e., working-mode or idling-mode) to assist the reduction of diffusion losses and emissions (U.S. EPA, 1995; 2008). Previous tests conducted by the EPA indicated that automatic lids could reduce solvent loss by a factor of 50 percent or more (U.S. EPA, 2008). The best emission reduction technique has been reported to be the minimization of cross-current drafts at the lip of the degreaser (Turner, 1992). In addition, enclosed and automated vapor degreasers offer the potential of significantly reducing air emission losses.

As an extension and further to this study, crossdrafts will be quantified under operating conditions and measured average crossdraft velocities will be documented at each site. Additionally, the results of ventilation and crossdrafts measurements, activity observations, and calculated emission factors will be evaluated. Further studies of this nature should focus on the development of emission factors from the results of emission rates. For future work of this magnitude, it is recommended that personal exposure monitoring of workers be conducted at each site and that other suitable devices for concentration measurement (e.g., photoionization detector with strip chart or digital recording capability) of both confined and fugitive vapors, sensitive to chlorinated solvents, but relatively insensitive to SF₆ and other interfering environmental factors over the entire range, should be used in conjunction with charcoal tube samples. Finally, enclosed and automated vapor degreasers are preferred to open-top models since they offer the potential for significantly reducing the use of solvent by preventing losses through air emissions.

ACKNOWLEDGMENT

We thank Dr. Richard Wadden, Dr. Peter Scheff, Dr. John Franke, and Dr. Charles Keil, for their invaluable support, reviews, and critique of the initial manuscript.

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